J Radioanal Nucl Chem (2011) 288:759–764
DOI 10.1007/s10967-011-0986-1

Electron beam induced degradation of clopyralid in aqueous solutions

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Received: 26 December 2010 / Published online: 15 February 2011

Abstract The degradation characteristics of clopyralid irradiated by electron beam (EB) was studied in aqueous solutions. The effects of factors, such as initial clopyralid concentrations, addition of radicals scavenger, initial solution pH and addition of H_2O_2, were investigated on clopyralid degradation efficiency and mechanism. It was found that the EB-radiolysis was an effective way to degrade clopyralid and its degradation rate decreased with the increasing of substrate concentration. In the investigated initial concentrations range of 100–400 mg L^{-1}, the radiolytic degradation of clopyralid followed a pseudo-first kinetic order. The results from addition of radicals scavenger indicated that both $^{\bullet}OH$ and e_{aq}^{-} played significant roles in the degradation of clopyralid. Furthermore, the alkaline condition and addition of H_2O_2 (<10 mM) in the solution also slightly enhanced the efficiency of clopyralid degradation. The ion chromatography analysis showed that some organic acids (formic acid, acetic acid and oxalic acid) were formed, while the completely dechlorination of the substrate was achieved and organic nitrogen was recovered in the form of ammonium and nitrate ions during the irradiation process.

Keywords Clopyralid · Electron beam · Radiolysis · Degradation

Introduction

There are a great variety of pesticides used in agricultural field worldwide for better quality and quantity of the crops every year. Their frequent use, chemical stability, resistance to biodegradation and solubility in water have resulted in their residues in various environmental matrices [1–5]. It is a pressing task to develop efficient methods for their removal and transformation to the products that are harmless to human and environment. As one of the advanced oxidation processes (AOPs), the radiation technology of EB and gamma-ray have showed great promise during the last three decades for efficient treatment of organic pollutants, especially for the thorough decomposition of biorefractory compounds [6–8]. Substantial work have also been done on the degradation of herbicides using radiation technology and their completely destruction were achieved after the treatment [9–12].

Clopyralid (3, 6-dichloro-2-pyridinecarboxylic acid) is a kind of systemic herbicide registered by USA–EPA for control of woody plants on rangeland and pastures. It also provides effectively for controlling annual and perennial broadleaf weeds in certain turf and crops. Figure 1 shows the molecular structure of clopyralid.

The half-life of clopyralid in soil can range from 15 to more than 280 days. Due to its high solubility in water and not adsorbed to soil particles, this herbicide may leach into groundwater and cause a potential threat to human [13]. It was reported that clopyralid was one of the herbicides that were often found in drinking water [2]. Thus, the treatment of clopyralid contaminated water is quite important especially for the production wastewater which contained high concentration of clopyralid.

Chen et al. [14] studied the treatment of wastewater from production process of clopyralid, and found that the resin adsorption process can remove about 99% of wastewater COD. However, the adsorption process did not degrade clopyralid, then a further treatment was also needed. Corredor et al. [13] researched the electron chemical

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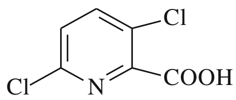
Fig. 1 Molecular structure of 3, 6-dichloro-2-pyridinecarboxylic acid



process in the reduction of the clopyralid herbicide using mercury electrodes, giving the results that the degradation of clopyralid had close relationship with its pK value and the pH in the solution. The electro-Fenton treatment of clopyralid in aqueous solution and photocatalysis degradation of clopyralid in TiO_2 suspended solution were also studied, and results demonstrated both of the reactions process followed a pseudo-first order kinetics [15, 16]. However, the degradation of clopyralid using radiation technology has never been reported.

The aim of this work is to study the degradation of clopyralid using radiation technology in aqueous solutions under various conditions. The effects of initial clopyralid concentrations, addition of radicals scavenger, initial solution pH and addition of H_2O_2 on the degradation rates of clopyralid were investigated. The by-products of the clopyralid degradation were analyzed using ion chromatography and further reaction mechanism was also discussed.

Materials and methods

Clopyralid was purchased from Matrix Scientific (>99% purity) without any further purification before use. *Tert*-butanol and acetonitrile were chromatographic grade, both obtained from Sigma. Formic acid (HCOOH), acetic acid (CH_3COOH), $H_2C_2O_4$, 85% H_3PO_4, 30% H_2O_2, NH_4Cl, NaOH, $NaHCO_3$, Na_2CO_3, HNO_3, KNO_3 and $HClO_4$ were analytical grade and purchased from Shanghai Chemical Reagent Co. Ltd. All the solutions in this experiment were prepared by deionised water (resistance >18.2 MΩ).

Radiolysis procedure

GJ-2-II electron accelerator (Shanghai Xianfeng electrical plant, China), providing a beam energy of 1.8 MeV and variable current (0–10 mA), was used as irradiation source with clopyralid samples placed in radiation field about 30 cm distance away. The current of EB was set as 1 mA in this study.

Clopyralid solutions of 300 mg L^{-1} were adopted as the synthetic wastewater (except for the investigation of initial concentrations), and the absorbed doses were range from 2 to 50 kGy. The solutions were saturated with air (except for the investigation of radicals scavenger) and without initial pH adjustment (except for the investigation of initial solution pH). For the influence of H_2O_2, 1–20 mM H_2O_2 were added in the clopyralid solutions.

Analytical methods

A high performance liquid chromatography (HPLC, Agilent 1200 series), equipped with a reversed phase column (C_{18}, 150 × 4.6 mm) and UV–Vis detector, was used to determine clopyralid concentrations before and after EB irradiation. The detector wavelength was set at 225 nm and a 10 μL sample was injected. The mobile phase was a mixture of acetonitrile and water (3:7, v/v) at a flow rate of 0.8 mL min^{-1}, and the water was acidified with 0.1% H_3PO_4.

The concentrations of chloride, ammonium, nitrate ions and organic acids released from radiolysis process were measured (10 μL samples were used) by ion chromatography (IC, Metrohm) with a METROSEP A SUPP 5-250 cationic ions exchange column and a METROSEP 2-250 anionic ions exchange column. For ammonium measurement, the mobile phase in the cationic column was 2 mM HNO_3 with a flow rate of 1 mL min^{-1}. The determination of formic acid, acetic acid, oxalic acid, chloride and nitrate ions in the samples was accomplished by anionic column where the mobile phase was a mixture of Na_2CO_3 (3.2 mM) and $NaHCO_3$ (1.0 mM) with a flow rate of 0.7 mL min^{-1}.

Results and discussion

Effect of initial clopyralid concentrations

The degradation of clopyralid solutions with its initial concentrations of 100–400 mg L^{-1} using EB-Radiolysis was studied. As shown in Fig. 2, the normalized clopyralid concentration (C/C_0) rapidly dropped with the raising of absorbed dose, and the increase of initial concentration

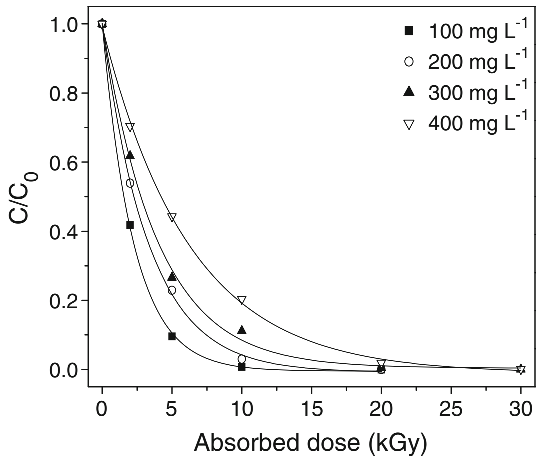


Fig. 2 Effect of initial clopyralid concentrations on its degradation rate

Table 1 The pseudo first-order dynamical equations and its correlation coefficients

Concentration (mg L^{-1})	$\ln C/C_0 = \ln A - BD$	R^2
100	$y = -2.0605x + 0.1086$	0.9995
200	$y = -2.8350x + 0.2839$	0.9926
300	$y = -3.5904x + 0.5194$	0.9875
400	$y = -4.3920x + 1.2778$	0.9871

resulted in the diminished degradation efficiencies. For example, at absorbed dose of 5 kGy, the degradation rates were 91, 87, 83 and 66% at initial clopyralid concentrations of 100, 200, 300 and 400 mg L^{-1}, respectively. At initial concentration of 400 mg L^{-1}, about 99.9% of clopyralid was removed at adsorbed does of 30 kGy. These results demonstrated that EB could efficiently degrade clopyralid.

As illustrated in Fig. 2, the clopyralid concentration exponentially decayed with the increasing of absorbed dose. Putting $\ln C/C_0$ and absorbed dose (D) into regressive analysis, taking A and B as constants in the equations, the results are presented in Table 1. The values of correlation coefficients were over 0.98, which indicated that the EB induced degradation of clopyralid followed pseudo-first order kinetics at different initial concentrations. It agreed well with the results from the other works using radiation technology to degrade organic pollutions where the kinetics in the degradation processes followed approximately a pseudo-first kinetic order [17, 18].

Degradation under air-saturated and nitrogen-saturated conditions

When aqueous solution was irradiated by high-energy electrons, the following main active species products were generated [6].

$$H_2O \rightarrow {}^{\bullet}OH\ (0.29\ \mu mol\ J^{-1}) + e_{aq}^{-}\ (0.29\ \mu mol\ J^{-1}) + {}^{\bullet}H\ (0.06\ \mu mol\ J^{-1}) \quad (1)$$

The numbers in parentheses indicate the radiolysis yields (G-values) in SI units. As well known, ${}^{\bullet}OH$, e_{aq}^{-} and ${}^{\bullet}H$ were high reactive radicals that can react with organic compounds and caused its degradation. On one hand, ${}^{\bullet}OH$ was an active particle with oxidation potential ($E_0 = 2.8$ V) that has a strong oxdative ability only followed fluorin ($E_0 = 3.2$ V), and it can efficiently oxidate the organic compouds in aquous solutions [19]. On the other hand, both the e_{aq}^{-} and ${}^{\bullet}H$ can deoxidize the targeted organic compounds, and the e_{aq}^{-} has a strong reductive ability ($E_0 = -2.9$ V) which can effectively dehalogen the halogenlated organic compounds [20].

In order to investigate which particle played the leading role in the degradation of clopyralid, *tert*-butanol was added to the N_2 saturated clopyralid solutions. When the solution was saturated with air, e_{aq}^{-} and ${}^{\bullet}H$ reacted rapidly with dissolved oxygen molecules forming $HO_2^{\bullet}/O_2^{\bullet}$ (reaction (2) and (3)). The ${}^{\bullet}OH$ was the main reactive species in the solution [21]. In N_2 saturated solution, ${}^{\bullet}OH$, e_{aq}^{-} and ${}^{\bullet}H$ all existed and should be considered in the reactions process [22], while in N_2 saturated solution containing 0.5 mol/L *tert*-butanol, ${}^{\bullet}OH$ and ${}^{\bullet}H$ were scavenged by *tert*-butanol (reaction (4) and (5)), and e_{aq}^{-} was the main reactive species in the clopyralid solutions [21].

$$e_{aq}^{-} + O_2 \rightarrow O_2{}^{-\bullet} \quad (2)$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad (3)$$

$${}^{\bullet}OH + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O \quad (4)$$

$$H^{\bullet} + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2 \quad (5)$$

As shown in Fig. 3, the higher degradation rate was achieved in N_2 saturated solutions and the lower degradation rate happened in N_2 saturated solutions containing 0.5 mol L^{-1} *tert*-butanol. It can come to a conclusion that both ${}^{\bullet}OH$ and e_{aq}^{-} played vital roles in the clopyralid degradation process. In AOPs, the ${}^{\bullet}OH$ was taken as the main reactive species to degrade organic pollutions, and the previous studies on the degradation of clopyralid by AOPs technology indicated the ${}^{\bullet}OH$ shown great reactivity in the process [15, 16].

Effect of initial pH

The initial pH is an important factor in the degradation processes since it influence the form of clopyralid and the numbers of some active species in aqueous solution. In this work, the effects of initial pH at 3, 7 and 11 at absorbed doses of 2, 5 and 10 kGy were investigated. As shown in

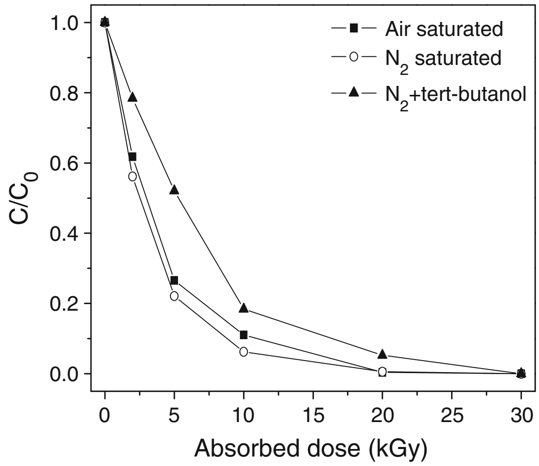


Fig. 3 Effect of radicals scavenger on the degradation of clopyralid (300 mg L^{-1})

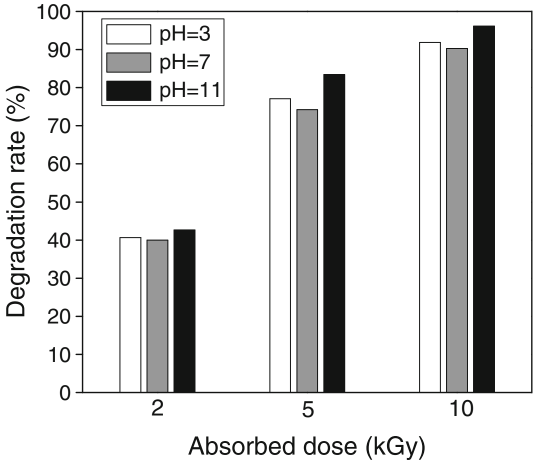


Fig. 4 Effect of initial pH on the degradation of clopyralid (300 mg L^{-1})

Fig. 4, the degradation rate was higher under basic condition than that in acidic and neutral conditions. In alkaline condition, $^\bullet H$ would be inverted into e_{aq}^- (reaction (6) [23].

$$H^\bullet + OH^- \rightarrow e_{aq}^- + H_2O \tag{6}$$

As one of the main reactive species to degrade clopyralid, more e_{aq}^- existed under basic condition from the reaction (6). In addition, the clopyralid in the form of ion in alkaline solutions may accelerate the degradation rate [13]. Thus, the solutions in basic environment may be helpful to the degradation of clopyralid.

Enhanced degradation by adding H_2O_2

The H_2O_2 is a well-known additive in AOPs because it can enhance the efficiency of treatment [24, 25]. A series of experiments were conducted for exploring the effect of added H_2O_2 on the clopyralid degradation efficiency. The H_2O_2 itself can not directly decompose the organic pollutions, but it can react with reactive particles forming new radicals that affecting the degradation rate [26]. Fig. 5 shows C/C_0 is a function of the added concentration of H_2O_2. The initial clopyralid concentration was set as 300 mg L^{-1} and the concentration of added H_2O_2 varied from 1 to 20 mM. As illustrated in Fig. 5, the C/C_0 declined as the concentration of H_2O_2 increased up to 10 mM, which may be explained by the following reaction [21]:

$$e_{aq}^- + H_2O_2 \rightarrow OH^- + {}^\bullet OH \tag{7}$$

A further addition of H_2O_2 resulted in slight increase of C/C_0. At a higher concentration of H_2O_2, the formation of $HO_2^\bullet$ and H_2O_2 can be important pathways for the scavenging of hydroxyl radical by the following reactions [21].

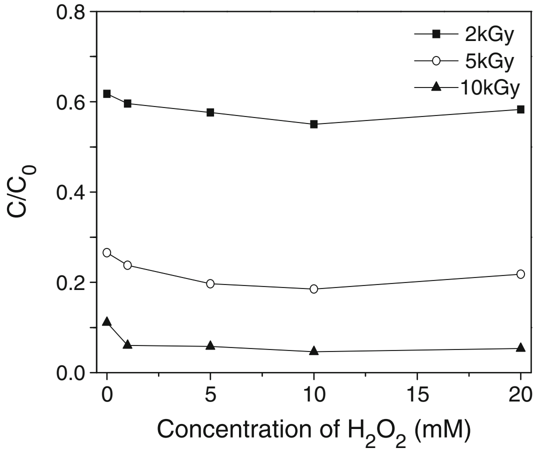


Fig. 5 Effect of H_2O_2 on the degradation of clopyralid (300 mg L^{-1})

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \tag{8}$$

$${}^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{9}$$

As a result, adding H_2O_2 at 10 mM was appropriate for optimizing the degradation rate of clopyralid. A further addition of H_2O_2 was not helpful to the enhanced degradation of clopyralid.

The formation of ions during the radiolysis process

The radiolysis degradation of herbicides was generally accompanied by the formation of some intermediates [27]. In this work, the HPLC analysis showed several byproducts formatted and disappeared as absorbed dose raised. The release of inorganic ions and some organic acids were detected by ion chromatography. Since clopyralid contains covalent bonded chlorine while e_{aq}^- is a high reactive species that can attack the chorine on the pyridine ring [20], the chloride would be released during the radiolysis process. As shown in Fig. 6, the formation of chloride was very fast in the absorbed dose before 20 kGy and kept in a relative stable level thereafter. It was calculated that about 99% chlorine was inverted into chloride after 20 kGy treatment. It can come to a conclusion that the destruction of clopyralid accompanied with the release of chloride during the irradiation process.

The organic nitrogen may be transformed into to N_2, NH_4^+ and NO_3^- during the degradation of clopyralid [16]. As can be seen from Fig. 6, the concentration of ammonium ion rapidly raised between 10 and 20 kGy of absorbed dose irradiation. At lower absorbed dose (<10 kGy), the destruction of the clopyralid may not accompany with the transformation of organic nitrogen. The ammonium was formatted later at a higher absorbed dose. The formation of nitrate ion was quite a little during the process due to the limited available oxygen in the solutions used for

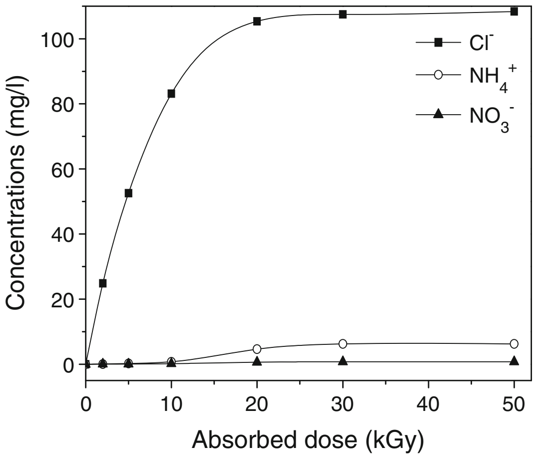


Fig. 6 The release of inorganic ions during the degradation of clopyralid (300 mg L^{-1})

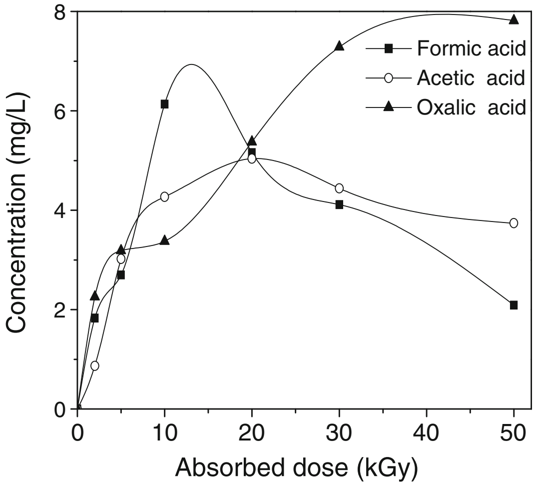


Fig. 7 The formation of organic acids during the degradation of clopyralid (300 mg L^{-1})

the convertion of organic nitrogen or ammonium into nitrate ion.

The organic acids are important byproducts during the degradation of organic pollutions [28]. In this research, three kinds of organic acids were detected which were formic acid, acetic acid and oxalic acid. As shown in Fig. 7, the formation of formic and acetic increased at lower absorbed dose (<20 kGy) and dropped after a higher absorbed dose irradiation. At a lower absorbed dose, the destruction of clopyralid accompanied with the accumulation of these two organic acids. The higher absorbed dose caused a further mineralization of formic and acetic acids or the formation of oxalic acid (two formic acid molecules forming one oxalic acid molecular). The concentration of oxalic acid in the solution increased during the whole process, and a further degradation need higher absorbed dose.

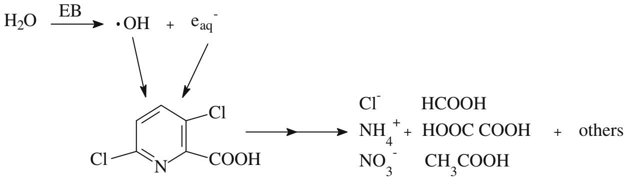


Fig. 8 The reaction scheme for clopyralid degradation in EB radiolysis process

From above analysis, the main reaction process followed the pathway below (Fig. 8).

Conclusions

The electron beam (EB) could effectively induce the degradation of clopyralid in aqueous solutions and the reaction process followed pseudo-first order kinetic. Both $^{\bullet}OH$ and e_{aq}^{-} played vital roles in the decomposition of clopyralid. The higher degradation rate realized under alkaline condition and addition of H_2O_2 (< 10 mM) in the solutions could further enhance the degradation efficiency. The clopyralid boned chlorine was converted into chloride and organic nitrogen was transformed into ammonium and nitrate ions in the irradiated solutions, and the formation of formic acid, acetic acid and oxalic acid were also accompanied. The formic and acetic acid decreased at a higher absorbed dose (>20 kGy) while the oxalic acid increased through the whole irradiation process.

Acknowledgments This work was financially supported by National Natural Science Foundation of China (No. 40973073, 4083 0744, 410973073, 11025526), Shanghai Leading Academic Discipline Project (No. S30109), and National Key Technology R&D Program in the 11th Five Year Plan of China (No. 2009BAA24B04), and Shanghai Municipal Foundation (No 09ZR1411300, 0953050 1200, 09XD1401800), who were gratefully acknowledged.

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